SUPERSONIC BEAM STUDIES OF CARBON CONDENSATION

R. E. Smalley
Rice Quantum Institute and Department of Chemistry
Rice University
Houston, Texas 77251

INTRODUCTION

In the course of the current rage of fascination with how diamond growth may be nucleated and controlled, it is probably wise to consider in some detail the nature of the beast with which diamond growth must compete. The beast in this case is the growth graphite either in its perfect crystalline form, or more typically in one of its less flat, often more tortuous morphologies. After all graphite is the most stable form of carbon under moderate pressure conditions, and diamond growth can dominate only as a result of some kinetic trick. Unfortunately, this will have to be a very powerful trick indeed, since it turns out that the kinetics of nucleation and growth of graphitic type objects are sensationally facile.

This short paper considers some of the newest evidence of just how formidable this graphitic beast is. Strangely, much of this new evidence has come from the rarified and esoteric environment of supersonic beams and laser spectroscopy. Advances in laser and supersonic molecular beam techniques over the past 5-10 years have produced a flood of new results and insights as to the nature of small clusters. Within the sub-field of strongly bound (non van der Waals) clusters, certainly one of the most active and intellectually exciting areas has been the study of carbon. Although many of these new experiments are still in the process of verification, extension, and further interpretation, a remarkable new picture is beginning to emerge as to some of the dominant processes of carbon condensation and the nature of the (largely graphitic) species involved.

Perhaps the most concise way to summarize this subject is simply to list some of the key features of the emerging new view of the small clusters of carbon.

(1) Carbon nucleates to form small clusters far more readily than any other element in the periodic table (including such refractory metals as tungsten and tantalum or the semiconductors silicon, germanium, and gallium arsenide).

(2) The smallest clusters (C_2 through C_{29}) are essentially one-dimensional: they are most stable in the form of linear chains or monocyclic rings (depending on the charge state and temperature).

(3) Even-numbered clusters in the 32-100+ atom size range often take the form of entirely closed, hollow spheroidal

shells (the "fullerenes") made up of catacondensed networks of 5- and 6-membered rings. All such fullerenes contain exactly twelve 5-membered rings. Under certain conditions it is possible to trap any of a wide range of metal atoms inside the hollow cavity of these fullerene shells. This includes such metals as sodium, potassium, cesium, calcium, barium, strontium, lanthanum, and actinides such as uranium.

(4) Odd-numbered clusters in the 33-101+ atom size range often take the form of nearly-closed spheroidal shells (the "semifullerenes") also made up of 5- and 6-membered rings.

(5) The prototypical fullerene, C_{60} ("buckminsterfullerene"), prefers the shape of a truncated icosahedron. Because of its size and perfect symmetry, it is extremely stable (chemically, thermodynamically, photophysically). The strain of closure of the fullerenes tends to concentrate at the vertices of the pentagons. Only for C_{60} -- and only when it takes the perfectly icosahedral form -- is this strain uniformly distributed over all carbon centers. It is this symmetry-derived absence of concentrated strain that gives C_{60} its unique stability.

(6) The fullerenes appear to be made whenever carbon condenses, including sooting flames where they are the most abundant ions present above 300 amu.

(7) A spiraling shell is an interesting model for the active nucleus involved in carbon grain growth in space, and soot formation in combustion environments here on earth. It is sensible that this is the most likely graphitic growth form possible in condensing carbon vapors. In this view the fullerenes are best interpreted as side products (dead ends) in a growth process that ultimately produces macroscopic particles.

When compared to the view prevalent in the carbon literature only a few years ago, these 7 points (with the possible exception of the first two or three) are quite divergent -- perhaps even wildly divergent. Nonetheless, my colleagues and I have found the new experimental evidence compelling. To our knowledge this picture is the only one consistent with all experimental results, both new and old.

Within the scope of this short paper it is unreasonable to attempt a full review of the various experiments and lines of argument that have led to this new view. My colleagues and I have published extensively as this work has proceeded from the original experiments of Rohlfing, Cox, and Kaldor (1), and our subsequent realization that C_{60} is supremely special and probably spherical (2). Two fairly comprehensive and up-to-date reviews have recently appeared as articles in the journal Science (3,4). These serve well as both a summary of current evidence and beliefs (at

least as perceived the principal proponents), and as pointers to the relevant literature.

Instead, I will take this opportunity to dwell a bit on one central point of this story that is often misunderstood: the mechanism we have come to suspect is responsible for the facile formation of C_{60} and the other fullerenes. Like most mechanisms offered to explain chemical reactions, this one is highly conjectural. But it does offer a simple explanation for why hollow, spheroidal objects form with such facility. I bring it up in the context of this symposium on diamond growth since the conditions used in most of the current diamond film research are also those where such spheroidal, basically graphitic objects as the fullerenes would be expected to form as well. The thrust of the argument is that this fullerene formation mechanism may either be the "beast" himself, or at least a close associate.

A NEW GROWTH SENARIO FOR THE FULLERENES AND GRAPHITIC SOOT

To most observers the most unbelievable aspect of the buckminsterfullerene story was not that C_{60} may prefer the soccerball geometry. It was clear from the outset that this was a perfectly kosher bonding network for carbon which solved the problem of tying up all dangling bonds with beautiful symmetry and structural integrity. In fact it had been predicted to be stable, and its synthesis had been undertaken years before the supersonic cluster beam experiments were even conceived of at Rice University. What seemed truly incredible was the notion that such a huge, highly symmetric structure could pop full-formed out of something so simple and mindless as a carbon vapor. Particularly vexing was the question of why any molecule would naturally form with a such a huge vacuous cavity in the center. Whatever happened to Nature's supposed abhorrence of a vacuum?

Confronted with the clear fact that, regardless of intuition, C_{60} and the fullerenes are produced readily, and the compelling evidence that they did have the spheroidal cage structure, we searched for a rational growth mechanism. The growth senario we began to advocate was first sketched briefly in a few paragraphs of a short paper we submitted late in 1985 (5).

It seemed clear that the key topological event must involve some inherent tendency of a growing polycyclic aromatic net to curl. We are accustomed to think of aromatic carbon nets as rigid, flat plates. Certainly the vast majority of known polycyclic aromatic compounds are indeed flat (at least at absolute zero). More insidiously, the molecular model kits used to teach modern chemistry have engendered this notion of rigid, flat sp^2 carbon frameworks as though it were a central dogma of structural chemistry. This is a great model for ordinary closed shell aromatic molecules, but that is certainly not what one is dealing with when a pure carbon vapor condenses. Carbon networks growing at high temperature in the absence of hydrogen will have a

large number of dangling bonds, so it is by no means clear that perfect sp^2 hybridization should apply.

Instead we noted that simply by incorporating a pentagonal ring in the periphery of a growing hexagonal net, at least one good new carbon-carbon bond will always be formed from what was previously two dangling bonds. This pentagon causes the net to curl out of plane, the added strain of curvature being offset by the increased bonding.

Following along on this notion that curvature in a growing graphitic net would be a natural consequence of a local incentive to minimize dangling bonds, we supposed that if one pentagon was good, two would be better. But as a second-order consideration it should be noted that two adjacent pentagonal carbon rings is hardly ever encountered as a stable aromatic structure in ordinary polycylic compounds (it is an antiaromatic cycle, and it concentrates strain). One should therefore expect a tendency for the growing graphitic sheet to incorporate pentagons offset from one another by intervening hexagons on the leading edge of the growth front.

That is basically all there is to the mechanism. There is a simple local tendency to minimize dangling bonds by incorporating pentagons on the growth front, and a weaker tendency to have these pentagons spaced by an intervening hexagon. Note that if followed perfectly, this simple growth rule forms a net which closes perfectly on itself -- it makes a C_{60} soccerball!

Under rapid growth conditions, with insufficient time and/or energy to anneal out mistakes and adhere slavishly to the lowest energy path, this mechanism would predict a wide range of fullerenes to form. Once formed, the absence of dangling bonds on these fullerenes effectively removes them from subsequent direct growth reactions. They can participate further in the condensation process only by adhering to each other, or by becoming sufficiently excited to break open at a site where strains have concentrated, thereby producing a point for further chemical attack and growth.

As we argued in the original paper (5), it seems likely that a rapidly growing graphitic net tying up dangling bonds by this simple rule will most typically fail to close. Instead it is easy to visualize one growth front curling over and burying the opposite edge inside to form the first turn of a 3-dimensional spiral. Once an edge is buried, there is no opportunity for the growth to stop, the spiral simply continuing to grow turn by turn until a macroscopic spherical carbon particle is produced. In fact such particles have been seen before with scanning electron microscopes (6). Such spherical carbon particles formed from pure condensing carbon we prefer to call "graphitic soot". Their ready formation is an unavoidable prediction of the fullerene growth mechanism.

CARBON GROWTH IN A HYDROGEN-RICH ENVIRONMENT

More relevant to the formation of ordinary soot in combustion environments -- and to the conditions where diamond film growth is sought in the experiments discussed in this symposium -- is the circumstance where there is a abundance of hydrogen. Since the fullerene growth mechanism we've been discussing is driven by the presence of dangling bonds, it's not immediately clear how it could apply when there is plenty of hydrogen around to tie up these dangling bonds. With enough hydrogen, one can make any graphitic sheet into a perfectly stable polycyclic aromatic hydrocarbon (PAH), and the most stable of these are always flat.

But at sufficiently high temperatures, hydrogen does not effectively tie up dangling bonds on carbon. Only another carbon atom can do that. Elementary chemical thermodynamics shows that most hydrocarbons are uphill with respect to graphite + H_2 even at room temperature. At the elevated temperatures encountered in flames this is even true for such species as methane and acetylene. The driving force for this is not so much the strength of the carbon-carbon bond in graphite. Instead it is primarily due the high entropy of gaseous H_2. Thermodynamically, that's why soot forms.

At elevated temperatures where a significant concentration of hydrogen atoms are present, the carbon-hydrogen bonds on the periphery of a PAH are not safe. Hydrogen abstraction reactions will proceed to generate a free H_2 molecule; leaving behind a bare, dangling bond on the now partially hydrogen terminated graphitic network. Under sufficiently intense H atom attack, therefore, the fullerene growth mechanism discussed above should come into play. The only way such a molecule can tie up its dangling bonds is to use carbon. It will do this until it forms a stable fullerene, or if it misses the fullerene stage, it would be expected to spiral its way to a microscopic soot particle.

So it is conceivable that the fullerenes and spiral graphitic soot particles may be formed in sooting flames. Indeed Homann and his group have found C_{60} and the fullerenes to be very abundant as positive ions in flames (7). In my opinion this is a singularly vital experiment to repeated and explored by other groups. Although currently the vast majority of the combustion community appears to disagree, to my reading the current evidence supports the notion that the fullerene growth mechanism is so facile in flames that it may be the mechanism responsible for the nucleation and early stages of soot growth in flames. Homann and his associates seem to have at least the beginnings of a method to give a critical test to this notion, but as yet there is no proof one way or the other.

FULLERENES UNDER DIAMOND GROWTH CONDITIONS

More relevantly to this symposium, it seems likely that fullerenes and the related graphitic spirals may be important species under diamond growth conditions. The conventional wisdom in the diamond film growth business is that graphitic (or "amorphous") carbon is constantly being nucleated as well as diamond on the growth surface, but that H atoms etch the non-diamond phases preferentially. The mechanism of this etching process is quite unclear, but there is little doubt that it is essential.

One obvious question is whether the etch process requires attack at an edge of a graphitic sheet. If it does, the presence of fullerenes will be a problem: they have no edges. In fact this suggests that an interesting line of research would be to study the susceptibility of large fullerenes to H atom attack. This turns out to be a vital issue in astrophysics as well. We have argued (2-4) that C_{60} in particular, and the fullerenes in general are likely to be made in vast quantities in the outer regions of carbon-rich red giant stars. Their abundance there, and their subsequent viability in space as they are driven from the star by photon pressure and the stellar wind will depend strongly on the ability to withstand H atom attack. It seems likely that there will be only a mild barrier to attaching a single H atom on one of the surface carbon atoms. But it may be a fairly weak bond, and do little to weaken the structural integrity of the fullerene cage. The lowest thermal dissociation process of such a H-fullerene would most likely be just a simple desorption of the H atom.

Beyond this question of getting rid of the fullerenes once formed, it is sobering consider the great efficiency of this fullerene condensation mechanism for carbon. Even in the absence of hydrogen, all the bare clusters of carbon starting from C_2, extending through the last of the linear chains and monocyclic rings, to the curling polycyclic graphitic nets, to the fullerenes and the spiraling soot particles ... all of these species are abnormally strongly bound molecules. Unlike any other element, these species are formed almost instantly in a laser-produced vapor, and the final end point, graphite, is one of the most refractory species known.

The fullerene growth mechanism when it defaults to the formation of a spiral graphitic soot particle quickly generates an almost perfect graphite particle. It is mostly edgeless: if it forms optimally, its only edges are found yon the last turn of the spiral, and on the innermost turn where the initial edge was buried. Since each layer of the spiral contains only 12 pentagons, the vast majority of the carbon atoms in such a structure are involved in hexagonal rings with only a tiny deviation from planarity. Remarkably, it turns out that the most perfect and symmetrical of these spiral soot particles (the one

that starts with an aborted C_{60} truncated icosahedron, and proceeds to a second layer of 240 atoms, a third of 540 atoms, etc.) naturally has each layer spaced from those above and below by 3.6 angstroms. This is almost exactly the normal interplanar spacing of bulk graphite. In other words, these spiral graphitic particles are macromolecular (but still microscopic) forms of graphite. They may be expected to form with extraordinary speed, and be highly stable. For diamond film growers this is a beast that, once conjured up, may be rather difficult to slay.

ACKNOWLEDGEMENT

REFERENCES

(1) Rohlfing, E. A., Cox, D. A., and Kaldor, A. J. Chem. Phys., 1984, 81, 3322.

(2) Kroto, H. W., Heath, J. R., O'Brien, S. C., Curl, R. F., and Smalley, R. E., Nature, 1985, 318, 162.

(3) Curl, R. F., and Smalley, R. E., Science, 1988, 242, 1017.

(4) Kroto, H. W., Science, 1988, 242, 1139.

(5) Zhang, Q. L., O'Brien, S. C., Heath, J. R., Liu, Y., Curl, R. F., Kroto, H. W., and Smalley, R. E., J. Phys. Chem., 1986, 90, 525.

(6) Iijima, S., J. Phys. Chem., 1987, 91, 3466.

(7) Gerhardt, Ph., Loffler, S., and Homann, K. H., Chem. Phys. Lett., 1987, 137, 306.